Integrated Water Quality and Aquatic Communities Protocol – Wadeable Streams

Standard Operating Procedure (SOP) #8: Water Chemistry, Sample Collection, and Processing

Draft Version 1.0

Revision History Log:

Previous Version	Revision Date	Author	Changes Made	Reason for Change	New Version

This SOP describes the process for the labeling, collecting, prepping, filtering, handling, and storing of water samples (for filtered water and Dissolved Organic Carbon [DOC]) to the laboratory. It also includes steps for field analysis of alkalinity.

All of the tasks associated with this protocol are highly susceptible to contamination or bias from mishandling. As with the other protocols, it is very important that the crew completely follow these protocols to avoid the introduction of contamination and error into the analyses. Special attention should be given to the use of gloves, filter handling, and general cleanliness. Field conditions, especially wind and gusts, can make this difficult. If there are issues caused by contamination or accidents, the sampling should be repeated.

The tasks are listed in the order they should occur: 1) Labeling, 2) Sample collection, 3) Filtration preparation, and 4) Filtering (metals/ions and DOC).

Labeling

Labeling is an important task and is a common source of mishandling specimens. All labeling of water chemistry (filtered, unfiltered, and DOC), should be followed in the following formats for consistency and accuracy. Ideally, vial and bottles are pre-labeled the night before or during transit using an electronic label machine (e.g., Brother Model PT-1400 or similar). Labels produced by these label makers are resilient, are always legible, weather resistant and do not fade or smear when exposed to solvents (especially Ethanol). The only caution is that they must be placed on a dry and clean surface (hence should be done first, before sample processing). Labels should always be placed on the vial or bottle, and not on the lids.

The following information should be included: stream name, stream code, park code, date (yyyymmdd format), sample type, and county/state. Stream names, stream codes, and counties are provided in a summary sheet given to the field crews prior to the start of the field season. Sample type is one of the following: Filtered water, unfiltered water, DOC, or Chlorophyll *a*. Examples of how labels should be laid out are presented in Figure 1.

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Figure 1. Preferred layout for labeling sample vials. This format should be used for all samples: Dissolved Organic Carbon (DOC), unfiltered, and filtered water.

If necessary (e.g., the batteries die or the label-maker breaks), labeling can be accomplished using colored vinyl tape (preferably white) and a permanent marker (e.g., Sharpie). The same information should be recorded as above in a legible manner.

Water Sample Collection

Water sample collection for streams is a relatively simple affair:

1. Ensure that the sample point is at a well mixed cross-section (done in SOP #7: Water Quality Multiprobe Calibration and Field Measurements).
2. Ensure that no crew members have entered the stream above the collection point.
3. Precondition the 2 L amber high density polyethylene collection vial by immersing the vial under the water surface, allowing approximately 0.5 L to enter. Loosely screw the lid and shake vigorously. This should allow some water to splash out the threads of the bottle.
4. Dump the preconditioning water away from the processing area.
5. Re-immerse the bottle at the sample point, allowing the water to completely fill the bottle. Cap the lid, place in the shade, and prepare for processing.

Note that at this point, it is allowable for the other crew members to enter the stream for sampling or other SOP work.

Prepping for Filtration

Set up for processing should be done in the shade, on level ground, and in a place with minimal loose debris. Shelter from wind is also ideal. A field towel should be laid out to provide a work surface relatively free from contaminants. The equipment for filtration should be clean and set up nearby.

Water Filtration

Depending on the analyses, water must be filtered and frozen to retard biological and chemical processes that can affect the chemical constituents in the time period between collection and analysis. This time period should not be more than 28 days, but the realities of field work, shipping samples, and the sample backlog of a chemical analytical lab dictate that this period may extend beyond 28 days. Hence, it is very important that samples be adequately filtered and

preserved to maintain sample integrity until analyzed. Holding times and methods for dealing with holding time exceedances are detailed in SOP #20: Quality Assurance Project Plan.

Because three different filter types are used (one for metals and nutrients, one for DOC, and one for Chlorophyll *a*; covered in SOP#11: Periphyton Collection), plastic storage bags containing the filters should be clearly labeled to avoid using an inappropriate filter for any specific sample processing.

Procedure for Cations/Anions (Filtered Water)

Water samples for cations/anions and nutrients are filtered through a 1.2 µm glass fiber filter (Whatman GF/C, Whatman product number 1822-047) into a 250 ml acid washed (SOP #1: Preparations, Equipment, and Safety) amber high density polyethylene (HDPE) bottle and frozen as soon as possible. Any changes in filtering mechanisms or filters should follow the procedures outlined in the QAPP (SOP #19: Quality Assurance Project Plan).

1. Using latex gloves and forceps, insert a clean, unused Whatman GF/C filter into the inline filter holder as shown in Figure 2. Assemble following the diagram and tighten the inflow fitting to the outflow fitting. Tighten until the body O-ring is compressed, and do not over-tighten. Make certain that the inflow fitting is a Luer fitting for attaching a Luer-lok syringe, and not a tube fitting.

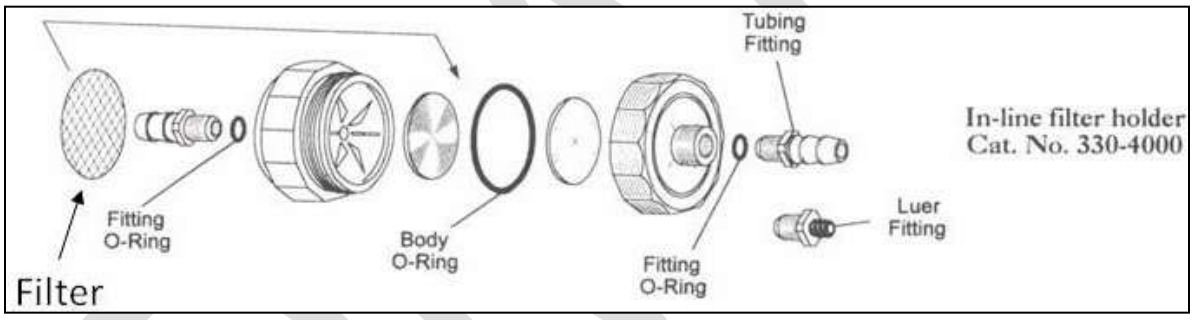

Figure 2. Diagram of inline filter holder (NALGENE®) showing assembly. In this configuration, the input is on the right (use the Luer fitting) and the outflow is on the left.

2. Using a 50 mL nylon syringe, draw 10 mL of sample water into the syringe. With the syringe inverted (i.e., plunger down, nozzle down), pull the plunger down until nearly removed from syringe body. Do not remove the plunger from the body of the syringe. Invert the syringe several times to pre-condition the syringe with sample water. Depress the plunger to expel the water onto the ground or into a waste container.

3. Draw up a full syringe of water from the sample being processed and attach the syringe to the filter holder using the Luer-Lok fitting. Precondition the filter and filter holder by depressing the plunger and expelling10 mL of water onto the ground or into a waste container.

4. Expel another 10 to 20 mL of the water into a properly labeled (see above) 250 mL sample collection bottle. Loosely attach the cap and gently shake the bottle. Dump the water onto the ground or into a waste container.

5. If any water remains in the current syringe, filter into the bottle. Refill the syringe with the sample water and continue to filter water until the bottle is filled. **Do not withdraw the syringe plunger while the syringe is still attached to the filter holder; the filter may shred inside.** Any headspace (air at the top of the bottle) in the bottle should be minimal (and ideally absent). Cap tightly.

6. Place the bottle in as cool and insulated a place as possible. This will generally be within the stream itself, using a cooler pouch with a reusable ice pack inside (within a mesh bag secured to the stream via a cord).

7. The filter holder should now be readied for filtering water for DOC analyses.

Procedure for Dissolved Organic Carbon

Dissolved organic carbon (DOC) analyses require that the sample be filtered through 0.7µm glass-fiber filters and contained in a 60 ml amber Boston Round glass vial. Glass vials and the filters should be prepared as in SOP #1: Preparations, Equipment, and Safety.

1. Sample water should be filtered following the above protocol for cations/anions and nutrients. Differences in the methods are simply the type of filter used (pre-washed 0.7 µm glass fiber filter; Whatman product number: 1825-047), the vial used (acid-washed and pre-combusted amber glass), and that the syringe does not need to be preconditioned (having been preconditioned in the above filtration).

2. Avoiding contamination is also crucial for DOC analyses. Skin oils, small soil particles, or litter particles could easily contaminate the sample. Likewise, any headspace in this vial can affect the analyses. The crew member should slowly top off the vial so that a convex meniscus is formed. Upon capping, this should eliminate any headspace.

3. The vial should then be stored in a cool and insulated place as described above.

Unfiltered Water Sample

Lastly, for total nutrients (including particulate matter), fill a 250 ml acid washed amber high density polyethylene (HDPE) bottle, making sure there is no headspace as described above. Store it in a cool place, as described above.

Procedure for Alkalinity Field Analysis

Alkalinity, or Acid Neutralizing Capacity, needs to be analyzed as soon as possible (recommendation is less than 24 hours). Alkalinity is measured in the field using a portable analytical kit. The general procedure is to add an acid to a sample and track the resulting change in pH. The amount of acid needed to achieve a certain pH is converted to the amount of alkalinity. Field analysis is identical in methodology to lab methodologies, except that a colorimetric endpoint (i.e., target color) is used to signal the target pH level.

The procedures below are for use with the Hach® Digital Titrator. If the alkalinity kit brand or style is changed or updated, data comparability procedures should be carried out following SOP #20: Quality Assurance Project Plan.

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Special Consideration: This test uses a titration cartridge of concentrated sulfuric acid (H_2SO_4). As a potentially dangerous substance, the crew will review the necessary Material Safety Data Sheet (MSDS) with the Project Lead and be familiar with all safety procedures before handling the kit. The minimum safety gear to be worn during analyses is: safety glasses and latex gloves. It is the responsibility of the Project Lead to ensure that crews have access to this gear.

1. Prior to analysis, an Erlenmeyer flask and graduated cylinder should be preconditioned with sample water.
2. Wear safety gear: gloves and eyewear.
3. Follow Hach protocol method 8203 for specifics on how to perform analysis (Appendix I). Use the below guidelines.
    a. Titrate to a pH endpoint of 4.8 (light violet-gray). **When assessing color, do not wear sunglasses.**
    b. Initial analyses should be performed using 100 mL of sample water and a Titrant Cartridge of 0.16 N H_2SO_4 (see Table 1 of Method 8203 in Appendix I).
4. Record amount of sample, strength of acid, and total digits.
5. Dispose of the waste into a 1 L plastic waste vial, clearly labeled "alkalinity waste."
6. Repeat steps 1 – 5. If the calculated value of alkalinity falls outside the 10 – 40 mg/L of CaCO3 range, the sample volume and titrant strength should be adjusted accordingly. If the initial acid strength used was wrong, or if the calculated value is more than10% off from the first measurement, or if the crew member thinks they missed the endpoint, repeat a third time.

If mistakes are made at any step of the way, the specific process must be repeated. On account of this, the crew must always have spare, uncontaminated equipment (e.g., acid washed vials, filters). The 2 L collection vial should allow ample water so that any particular sampling process can be repeated, without the collection of a new sample (the original collection point will be contaminated by other crew working on other SOPs).